

Advanced Organic Chemistry

SECOND
EDITION

Part B: Reactions and Synthesis

FRANCIS A. CAREY
and RICHARD J. SUNDBERG

*University of Virginia
Charlottesville, Virginia*

PLENUM PRESS • NEW YORK AND LONDON

Library of Congress Cataloging in Publication Data

Carey, Francis A., 1937-

Advanced organic chemistry. Part B, Reactions and synthesis.

Bibliography: p.

Includes index.

1. Chemistry, Organic. I. Sundberg, Richard J., 1938-. II. Title.

QD251.2.C36 1983

547.2

83-6278

ISBN 0-306-41088-5

ISBN 0-306-41199-7 (pbk.)

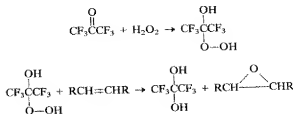
© 1977, 1983 Plenum Press, New York
A Division of Plenum Publishing Corporation
233 Spring Street, New York, N.Y. 10013

All rights reserved

No part of this book may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording, or otherwise, without written permission from the Publisher

Printed in the United States of America

of these reagents, nor similar combinations, are as generally useful as the more

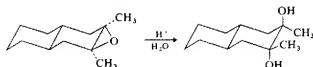


accessible peroxydicarboxylic acids, they do serve to illustrate the point that epoxidizing activity is not unique to the "peracids."

10.2.3. Subsequent Transformations of Epoxides

Epoxides are useful synthetic intermediates and the conversion of an alkane to an epoxide is often a part of a more extensive molecular transformation. In many instances the molecule remains at the oxidation level of the epoxide, but advantage is taken of the high reactivity of the epoxide ring to attain new functionality. These two- or three-step operations can accomplish a specific oxidative transformation of the alkene which would be impossible or more difficult to accomplish by a single-step oxidation. We will consider some of these transformations at this point. Scheme 10.6 provides a preview of the type of reactivity to be discussed.

Epoxidation may be preliminary to solvolytic or nucleophilic ring opening in synthetic sequences. In acidic aqueous media, epoxides are opened to give diols by an *anti* addition process. In cyclic systems, ring opening occurs to give the *trans* diol. Base-catalyzed epoxide ring openings, in which the nucleophile provides the



Ref. 52

driving force for ring opening, usually involve breaking the bond to the less substituted carbon, since this is the position most open to nucleophilic attack.⁵² The situation in acid-catalyzed reactions is more complex. The bonding of a proton to the oxygen weakens the C-O bond, facilitating its rupture by weak nucleophiles. If the C-O bond is largely intact at the transition state, the nucleophile will become attached to the less substituted position for the same steric reasons that were cited in the case of nucleophilic ring opening. If, on the other hand, C-O rupture is nearly complete when the transition state is reached, the opposite orientation will

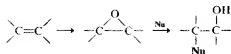
52. B. Rickborn and D. K. Murphy, *J. Org. Chem.* **34**, 3209 (1969).

53. R. E. Parker and N. S. Isaacs, *Chem. Rev.* **59**, 737 (1959).

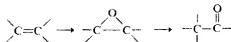
Scheme 10.6. Multistep Synthetic Transformations via Epoxides

SECTION 10.2
ADDITION OF
OXYGEN AT
CARBON-CARBON
DOUBLE BONDS

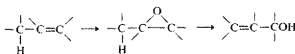
A. Epoxidation Followed by Nucleophilic Ring Opening



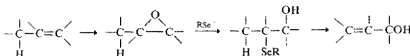
B. Epoxidation Followed by Rearrangement to a Carbonyl Compound



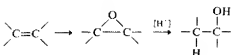
C. Epoxidation Followed by Ring Opening to an Allyl Alcohol



D. Epoxidation Followed by Ring Opening and Elimination



E. Epoxidation Followed by Reductive Ring Opening



be observed because of the greater ability of the more substituted carbon to bear the developing positive charge. When simple aliphatic epoxides such as propylene

